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(54) FLAME-RETARDANT STYRENE RESIN COMPOSITION

(57)Abstract:

PURPOSE: To improve the flame retardance of a styrene resin by compounding it with a specific halogenated bisphenol A and a brominated diphenylalkane as flame retardants and an auxiliary flame retardant in a specified wt. ratio.

CONSTITUTION: 100 pts.wt. high-impact styrene resin (e.g. a rubber-modified PS or ABS), 2-50 pts.wt. halogenated bisphenol A (e.g. tetrabromobisphenol A) having a halogen content of 35 wt.% or higher [flame retardant (I)], 0.5-30 pts.wt. brominated diphenylalkane (e.g. a brominated diphenylethane) having a bromine content of 50 wt.% or higher [flame retardant (II)] in a wt. ratio of (I)/(II) of 0.1-10, 1-30 pts.wt. auxiliary flame retardant [e.g. Sb₂O₃, Fe₂O₃, Al(OH)₃, borates, etc.], and if necessary 1-20 pts.wt. chlorinated polyethylene having a chlorine content of about 20-50 wt.% are compounded, melt mixed and kneaded at about 150-300°C with a twin-screw extruder, etc., and pelletized, thus giving a flame-retardant styrene resin compsn.

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CLAIMS

[Claim(s)]

[Claim 1] (A) Styrene resin As opposed to the 100 weight sections (B1) Below halogenation bisphenol A [of 35 % of the weight or more of halogen contents] made into a flame retarder (I) 2 - 50 weight section and (B-2) Below bromination diphenyl alkanes [of 50 % of the weight or more of bromine contents] made into a flame retarder (II) 0.5 - 30 weight section and (C) It comes to blend the fire-resistant assistant 1 - 30 weight sections, and they are (a flame retarder I) / flame retarder (II). A weight ratio Fire-resistant styrene-resin constituent characterized by being 0.1-10.

[Claim 2] Styrene resin Fire-resistant styrene-resin constituent according to claim 1 which comes to blend halogenation bisphenol A [flame retarder (I)] 4 - 30 weight section to the 100 weight sections.

[Claim 3] Styrene resin Fire-resistant styrene-resin constituent according to claim 1 or 2 which comes to blend bromination diphenyl alkanes [flame retarder (II)] 1 - 20 weight section to the 100 weight sections.

[Claim 4] A fire-resistant assistant 3 oxidization 2 antimony (Sb 2O₃) and 5 oxidization 2 antimony (Sb 2O₅), An iron sesquioxide (Fe 2O₃), borates, a magnesium hydroxide [Mg (OH)₂], and aluminum hydroxide [aluminum (OH)₃] from -- it was chosen -- at least -- a kind -- it is -- and the loadings -- styrene resin 100 Fire-resistant styrene-resin constituent of the claim 1-3 which is 4 - 12 weight section to the weight section given in any 1 term.

[Claim 5] Styrene resin Fire-resistant styrene-resin constituent of the claim 1-4 which comes to blend a chlorinated polyethylene 1 - 20 weight sections further to the 100 weight sections given in any 1 term.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the fire-resistant styrene-resin constituent which is equipped with good fire retardancy, tensile strength, a drop test impact strength, and shock resistance, and has the outstanding thermal resistance and weatherability.

[0002]

[Description of the Prior Art] although the former to styrene-resin constituents are various fields of an electric product and were broadly used from the outstanding mechanical characteristic and electrical property -- recently, TV, CRT, various computers, OA equipment, home electronics, etc. -- receiving -- UL94 of you ERU specification After being specified that it should conform to fire-resistant predetermined specification, flameproofing of styrene resins, such as an acrylonitrile-styrene-butadiene-rubber (namely, ABS) resin, comes to be attained, and generally they are halogen system flame retarders, such as a bromination diphenyl ether (for example, decabromodiphenyl ether, octabromodiphenyl ether), and 3 oxidization 2 antimony (Sb 2O3) as the method. The method of blending with a styrene resin is used widely.

[0003] However, the resin which blended the bromination diphenyl ether has the problem which the dioxin said for toxicity to be strong generates, when it burns considering the time of use of the moldings, or this as waste at the time of fabrication of the flame retardant resin with which weatherability is not only poor, but generally blended the bromination diphenyl ether. For example, even if physical properties use very good decabromodiphenyl ether as the aforementioned bromination diphenyl ether, there is a defect in which weatherability is not good. Moreover, if only the tetrabromobisphenol A adopted widely is used, since the thermal resistance of a moldings also falls sharply, weatherability is not not only good, but it will receive a remarkable limit on a use.

[0004] In order to solve these problems, tetrabromobisphenol A and a bromination epoxy resin are used together to JP,59-19148,B, and the method of blending with ABS plastics by making this into a flame retarder is indicated. Although this flame retarder can raise the weatherability of ABS plastics, cost is high, and also there is a fault to which a fluidity falls and use is restricted.

[0005]

[Problem(s) to be Solved by the Invention] this invention aims at offering the fire-resistant styrene-resin constituent which is equipped with good fire retardancy, tensile strength, a fall impact strength, and shock resistance, and has the outstanding thermal resistance and weatherability in view of the trouble in the aforementioned conventional fire-resistant styrene-resin constituent.

[0006]

[Means for Solving the Problem] It is this invention in order to attain the aforementioned purpose (A). Styrene resin As opposed to the 100 weight sections (B1) Below halogenation bisphenol A [of 35 % of the weight or more of halogen contents] made into a flame retarder (I) 2 - 50 weight section and (B-2) Below bromination diphenyl alkanes [of 50 % of the weight or more of bromine contents] made into a flame retarder (II) 0.5 - 30 weight section and (C) It comes to blend the fire-resistant assistant 1 - 30 weight sections, and they are (a flame retarder I) / flame retarder (II). A weight ratio The fire-resistant styrene-resin constituent characterized by being 0.1-10 is offered. And when the chlorinated polyethylene of a proper quantity is further blended with the styrene-resin constituent concerned, it is much more desirable.

[0007] styrene resin (A) used for this invention As the monomer, a styrene system monomer, for example, styrene, an alpha methyl styrene, Preferably a kind chosen from o-methyl styrene, p-chloro styrene, 2 and 4, 6-TORIBUROMO styrene, etc. or two or more sorts of mixture, and a styrene system monomer 40% of the weight or more 50 % of the

weight or more, The monomer in which these copolymerization is possible, for example, acrylonitrile, a methacrylonitrile, The styrene system polymer which comes to copolymerize a methyl methacrylate, an ethyl methacrylate, a maleic anhydride, N-phenyl maleimide, etc., Furthermore, the shock-proof resin which denaturalized these polymer by the rubberlike substance, such as for example, polybutadiene system rubber, ethylene-propylene rubber (EPDM etc.), and acrylic-ester system rubber, is meant.

[0008] Especially the rubber modified resin of the styrene system polymer which there are rubber denaturation polystyrene, ABS plastics, an AES resin, an AAS resin, a MBS resin, a rubber denaturation styrene-maleic-anhydride copolymerization resin, etc. as these shock resistance resin, for example, was made to carry out copolymerization of other copolymerization components, for example, phenyl maleimide, an alpha methyl styrene, TORIBUROMO styrene, the methyl methacrylate, etc. styrene like ABS plastics and an AES resin, acrylonitrile, and if needed, and was obtained is desirable.

[0009] What was manufactured by adding and carrying out the graft copolymerization of the monomer which can be copolymerized to the aforementioned rubberlike substance as a shock-proof resin used for this invention a styrene system monomer and if needed may be used as it is, or the obtained graft polymer which carried out graft polymerization, and the styrene system polymer which does not contain rubber may be mixed and used.

[0010] There is a method (for example, method of giving a suspension polymerization, after performing a bulk polymerization) which combined suitably a bulk-polymerization method, a solution polymerization method, an emulsion-polymerization method, suspension-polymerization methods, and these graft polymerization methods among the methods of manufacturing a graft polymer. Generally the content ratio of the rubberlike substance used for graft polymerization is 10 - 80% of the weight of a graft polymer, and the remainders are a styrene system monomer and this, and the monomer to copolymerize. The aforementioned shock-proof resin Although the rubberlike substance used in order to manufacture the 100 weight sections is generally 5 - 40 weight section, in order to maintain tensile strength and shock-proof balance, 7 - 35 weight section is desirable.

[0011] As a desirable example of the aforementioned styrene system polymer used for this invention, AS system resin, Namely, acrylonitrile, styrene, and other copolymerization components added if needed for example, N-phenyl maleimide, an alpha methyl styrene, and dibromo styrene -- TORIBUROMO styrene, a methyl methacrylate, a maleic anhydride, the polymer that copolymerized methacrylic-acid ******, Or MS system resin, i.e., a methyl methacrylate, styrene, and the polymer that copolymerized the copolymerization components (for example, N-phenyl maleimide, TORIBUROMO styrene, a maleic anhydride, a methacrylic acid, etc.) of others which are added if needed are mentioned.

[0012] These AS system resins and MS system resin are manufactured by the various polymerization methods of the aforementioned graft polymer, and the same method.

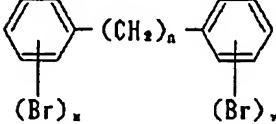
[0013] It is blended into a styrene resin, and the halogen content is 35 % of the weight or more, and its 45 - 63 % of the weight is [halogenation bisphenol A [a flame retarder (I) used by this invention (B1)] especially desirable. The styrene-resin constituent the halogen content of this flame retarder (I) excelled [constituent] 35 % of the weight in the low case at fire retardancy is not obtained. And similarly (B-2) bromination diphenyl alkanes [a flame retarder (II) used by this invention are blended into a styrene resin, the content of the bromine is 50 % of the weight or more, and it is especially desirable that it is about 75 - 85 % of the weight. Unless it fills the bromine content of this flame retarder (II) to 50% of the weight, the fire-resistant styrene-resin constituent excellent in the aforementioned (flame-retarder I) said appearance cannot be obtained.

[0014] The typical compound of the flame retarder (I) used for this invention is tetrabromobisphenol A, and this tetrabromobisphenol A brominates bisphenol A with a bromine, and is manufactured. As a concrete thing of other flame retarders (I) which can be used by this invention, tetrapod chloro bisphenol A, the tetrabromo bisphenol F, and the dibromobis phenol A are mentioned.

[0015] What is expressed with the following structure expression as an example of the flame retarder (II) used by this invention is mentioned.

[0016]

[Formula 1]



[0017] n is the number of 1-10 among [formula, and x and y are numbers with which x+y is set to 4 $\leq x+y \leq 10$.]

the typical compound expressed with the above-mentioned structure expression -- a bromination bibenzyl -- it is -- this bromination bibenzyl -- for example, methylene chloride and a bibenzyl -- a bromine -- the inside of a reaction vessel -- putting in -- still more nearly special bromination catalyst, for example, an aluminum chloride, (AlCl₃) And/or, aluminium bromide (AlBr₃) etc. -- it puts in and is manufactured by the *** method of promoting a bromination reaction

[0018] The amount of the flame retarder (I) used is a styrene resin (A). 100 It is 2 - 50 weight section to the weight section, and 4 - 30 weight section is especially desirable. If fire retardancy is inadequate in the amount of this flame retarder (I) used being under 2 weight sections and 50 weight sections are exceeded, shock-resistant intensity and thermal resistance will become inadequate. on the other hand -- flame retarder (II) the amount used receives the styrene-resin (A) 100 weight section -- it is 0.5 - 30 weight section, and 1 - 20 weight section is especially desirable. This flame retarder The amount used (II) A fluidity will become inadequate, if thermal resistance and weatherability are inadequate in their being under the 0.5 weight sections and 30 weight sections are exceeded.

[0019] 0.1-10 do and, as for the combination weight ratio of the aforementioned (flame retarder I) / flame retarder (II), 0.5-5 are the most desirable. And both ratio If less than 0.1 are insufficient as for a fluidity and 10 is exceeded, a fall impact strength, a heat deflection temperature, and temperature-increase-by-plastic-working stability will become clearly poor. the aforementioned flame retarder (I) and flame retarder (II) usually -- the shape of powder and a piece -- or -- as granular -- styrene resin (A) It is used blending.

[0020] In order to acquire fire retardancy sufficient in this invention, a fire-resistant assistant is used. as a fire-resistant assistant -- 3 oxidization 2 antimony (Sb 2O₃), 5 oxidization 2 antimony (Sb 2O₅), an iron sesquioxide (Fe 2O₃), borates, a magnesium hydroxide [Mg (OH)₂], and aluminum hydroxide [aluminum (OH)₃] from -- at least one sort of selected compounds are used The amount used is a styrene resin (A). 100 It is 1 - 30 weight section to the weight section, and 4 - 12 weight section is [2 - 20 weight section is especially good, and] the most desirable.

[0021] In this invention, if an impact strength can be raised more, the effect that the amount of this chlorinated polyethylene used raises an impact strength under in 1 weight section will run short, when a chlorinated polyethylene (CPE) 1 - 20 weight sections are further blended to the styrene-resin (A) 100 weight section, and 20 weight sections are exceeded, tensile strength will become poor. This chlorinated polyethylene has the most desirable thing of 1 - 45% of crystallinity, and 20 - 50 % of the weight of chlorine contents in the meaning which raises an impact strength.

[0022] Generally the halogen atom contained in a bromine system compound, a chlorinated polyethylene, etc. tends to separate with the gestalt of a hydrogen halide in the case of heating, and this hydrogen halide promotes degradation of a fire-resistant styrene resin, and remarkable heat discoloration is caused. It is a styrene resin (A), using as a thermostabilizer the hydrogen-halide absorbent which usually contains a metallic-soap metallurgy group oxide, an organotin compound, etc. in a styrene-resin constituent in this invention, in order to suppress or prevent such a phenomenon. 100 As opposed to the weight section 0.1-10 weight section addition is carried out.

[0023] Moreover, the styrene-resin constituent of this invention accepts the need, and is a styrene resin (A) 100 about a phenol system antioxidant, the Lynn system stabilizer, a sulfur system antioxidant, lubricant (for example, low-molecular-weight-polyethylene paraffin, an organic polysiloxane, the metal salt of a higher fatty acid, a higher-fatty-acid amide system compound, etc.), a dispersant, a weathering agent, an ultraviolet ray absorbent, a light stabilizer, etc. 0.01-7 weight section addition is carried out to the weight section.

[0024] The resin constituents of this invention are a styrene resin, a flame retarder (I) and a flame retarder (II), a fire-resistant assistant, and a thing that comes to contain 3 oxidization 2 antimony preferably, and comes to add a chlorinated polyethylene to this preferably. Furthermore, the resin constituent which added the hydrogen-halide absorbent, the phenol or the sulfur system antioxidant, the ultraviolet ray absorbent, etc. if needed, and was equipped with the predetermined property is obtained. In order to improve the moldability of thermoplastics moreover, the light stabilizer, the bulking agent, the coloring agent, the lubricant, plasticizer, and antistatic agent of optimum dose may be added, or you may mix the resin for polymer alloys, for example, a polycarbonate, a polyamide, polyester (PET, PBT, etc.), a polyphenylene ether, a polyvinyl chloride, a polymethyl methacrylate, an ethylene-methyl-methacrylate copolymer, polypropylene, a styrene-butadiene block copolymer, a hydrogenation acrylonitrile-butadiene copolymer, a hydrogenation styrene-butadiene block copolymer, etc. Generally the loadings are the 5 - 200 weight section to the styrene-resin (A) 100 weight section.

[0025] in order to obtain the styrene-resin constituent of this invention, after carrying out dryblend using the mixer like a Henschel mixer or a ribbon blender generally used in the field of synthetic resin as the mixed method, usually melting kneading is carried out by the extruder, the kneader, or the Banbury mixer further, for example

[0026] Since pyrolysis or a dehydrohalogenation reaction will be caused if an elevated-temperature operation is given

to the styrene-resin constituent of this invention when carrying out melting kneading among the above mixed methods, or when fabricating by the below-mentioned forming method, it is desirable to carry out in the range of 150 - 230 **. [0027] And when fabricating using the styrene-resin constituent of this invention, generally an injection-molding method, an extrusion method, compression forming, a blow molding method, etc. are applied.

[0028]

[Example] Although an example is given and this invention is explained in detail hereafter, the range of this invention is not restricted only to these examples. Moreover, all of the section in an example and % are based on a weight.

[0029] example 1 ABS-plastics [brand-name: -- the poly rack (Polylac) -- PA-747 and acrylonitrile 22% -- The styrene 57% and butadiene 21% and average rubber particle size of 0.31 micrometers, Tsi May Corporation], Tetrabromobisphenol A [a flame retarder (I)] of 59% of bromine contents, a deca BUROMO bibenzyl [a flame retarder (II)], and Sb 2O3 The amount shown in Table 1, respectively, Dibutyltin maleate which is a thermostabilizer Cylinder temperature after carrying out the dryblend of the 1.0 sections by the Henschel mixer together 200 to 210 degree C, and die-head temperature 2 shaft extruding press machine with a vent set as 220 degrees C. By extruding, the fire-resistant pellet-like styrene-resin constituent was obtained.

[0030] About the aforementioned granular fire retardancy styrene-resin constituent, they are ASTM 1709 and ASTM. D-638, ASTM D-648, ASTM D-256 (with a notch) ASTM D-1238 and UL-vertical firing examination (1/16 inch in thickness) Method. It examined about a fall impact strength, tensile strength, a heat resistance test (heat deflection temperature), the Izod (Izod) impact test, a fluidity, fire retardancy, thermal stability, and weatherability, respectively. The result is shown in Table 1.

[0031] In addition, while performing injection molding under fixed conditions, the method of the aforementioned heat instability test compares the hue of the test piece which put in the examination resin in the cylinder of an injection molding machine, it was made to pile up in the state of melting for 10 minutes, and fabricated it with the hue of the test piece directly examined by un-piling up, and evaluates the result as follows.

O :-discoloration-less **: -- a little -- xwith discoloration: -- it becomes yellow -- again -- the aforementioned weathering test -- a test piece -- WEZARO meter 100 hours -- and it is exposed for 150 hours, change of the hue is observed, and evaluation distinction of the result is carried out as follows

O : -- discoloration -- not carrying out -- **: -- become the xx:yellowish brown color colored x:yellow colored yellow a little [0032]

[Table 1]

試験番号	比較品	本発明品			比較品				
		1	1	2	3	2	3	4	5
ABS樹脂 (部)	100	100	100	100	100	100	100	100	
難燃剤 (I) (部)	22	18	12	6	24	1	1	10	
難燃剤 (II) (部)	0	3	7	11	0.2	20	5	35	
難燃剤 (I) / 難燃剤 (II)	—	6	1.7	0.5	120	0.05	0.2	0.29	
Sb ₂ O ₃ (部)	7	7	7	7	7	7	7	7	
物性	落下衝撃強度 (kg cm)	250	260	265	270	250	285	325	240
	引張強度 (kg/cm ²)	382	375	372	371	380	368	432	373
	熱変形温度 (°C)	73	79	83	85	74	88	92	81
	衝撃強度 (kg·cm/cm)	15	15	15	16	15	17	25	13
	流動性 (g/10min)	6	5.3	3.8	2.9	5.8	0.2	0.9	0.05
	難燃性 (UL-燃焼試験)	V-0	V-0	V-0	V-0	V-0	HB	V-0	
	熱安定性	×	○	○	○	×	○	△	○
	耐候性	△	○	○	○	○	○	○	

[0033] Example 2 ABS-plastics [poly rack (Polylac) PA-747], The same tetrabromobisphenol A [a flame retarder (I)] and same deca BUROMO bibenzyl [a flame retarder (II)] as the aforementioned example 1, and Sb 2O3 And it blended in the amount which shows the chlorinated polyethylene (CPE) of 2% of degree of crystallinity, and 35% of chlorine

content in Table 2, respectively, the fire-resistant styrene-resin constituent was obtained like the example 1, and it examined still like the example 1. The result is shown in Table 2.

[0034]

[Table 2]

試験番号	本発明品			
	4	5	6	
A B S樹脂 (部)	100	100	100	
難燃剤 (I) (部)	12	12	12	
難燃剤 (II) (部)	7	7	7	
難燃剤 (I) / 難燃剤 (II)	1.7	1.7	1.7	
C P E (部)	0	2.5	5	
Sb ₂ O ₃ (部)	7	7	7	
物性	落下衝撃強度 (kg cm)	265	270	280
	引張強度 (kg/cm ²)	365	360	358
	熱変形温度 (°C)	83	82	82
	衝撃強度 (kg·cm/cm)	15	18	20
	流動性 (g/10min)	3.8	3.4	2.9
	難燃性 (UL-燃焼試験)	V-0	V-0	V-0
	熱安定性	○	○	○
	耐候性	○	○	○

[0035] Various styrene resins shown in example 3 table 3 (A) The same flame retarder (I) and same flame retarder (II) as the aforementioned example 1, and Sb₂O₃ And the same CPE as the aforementioned example 2 was blended with the dibutyltin maleate 1 section in the amount shown in Table 3, respectively, and by the same method as an example 1, the fire-resistant styrene-resin constituent was obtained and it examined still like the example 1. The result is shown in Table 3.

[0036]

[Table 3]

試験番号	本発明品			
	7	8	9	
スチレン系樹脂	S ₁ (部)	100	0	0
	S ₂ (部)	0	100	0
	S ₃ (部)	0	0	100
難燃剤 (I)	(部)	12	11	12
難燃剤 (II)	(部)	7	6	7
難燃剤 (I) / 難燃剤 (II)		1.7	1.8	1.7
Sb ₂ O ₃	(部)	7	7	7
CPE	(部)	5	5	5
物性	落下衝撃強度 (kg cm)	285	295	275
	引張強度 (kg/cm ²)	358	355	352
	熱変形温度 (°C)	82	83	86
	衝撃強度 (kg·cm/cm)	20	21	17
	流動性 (g/10min)	2.9	2.7	3.5
	難燃性 (UL-燃焼試験)	V-0	V-0	V-0
	熱安定性	○	○	○
	耐候性	○	○	○

<注>

S₁: ポリラック (Polylac) PA-747S₂: AES樹脂 (アクリロニトリル20%、スチレン56%、EPDM 24%、平均ゴム粒径 0.3 μm)S₃: ABS樹脂 (アクリロニトリル18%、スチレン50%、N-フェニルマレイミド2%、α-メチルスチレン3%、メタクリル酸メチル2%、ブタジエン25%、平均ゴム粒径 0.3 μm)

[0037]

[Effect of the Invention] The fire-resistant styrene-resin constituent of this invention had good fire retardancy, tensile strength, a fall impact strength, and shock resistance, and is equipped with the outstanding thermal resistance and outstanding weatherability, and there is a merit that the fabricating operation of the moldings excellent in the mechanical characteristic can be carried out easily.

[Translation done.]